# Inorganic Combinatorial Materials Science Programs in Japan


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# Combinatorial Materials Science

• When Japanese scientists speak of materials property measurement, optimization or discovery, they do not use the word "combinatorial" – *it is automatically assumed, as there is no other viable approach for the investigation of complex materials systems*.

• The Japanese Ministry of Science and Education has identified combinatorial materials methodologies as essential to the technological future of the country.

# Japan Visit, February 2004

| Location | Scientists Visited | Materials Class | Specific Materials | Combinatorial Synthesis Technique | Combinatorial Analysis Techniques (Primary) |
|---|---|---|---|---|---|
| Tokyo Institute of Technology[a] | Prof. Hideomi Koinuma[b]<br>Dr. K. Itaka<br>Prof. Yuji Matsumoto<br>Mr. Ryota Takahashi<br>Mr. Ken Hasegawa | Thermoelectrics | $(Ca_{1-x}A_x)_3(Co_{1-y}B_y)_4O_9$<br>A=Mg, Sr, Ba, Ag, Bi<br>B=Zn, Cu | PLD[c] | PF[d], XRD |
| | | Organic Semiconductors | Pentacene/$Al_2O_3$ | MBE (graded thickness) | Ellipsometry |
| | | High $T_c$ fluxes | $CuO_x$–$BiO_x$–$Bi_4Ti_3O_{12}$ | PLD | RHEED |
| | | Transparent Magnetic films | $TiO_2$:M<br>M = transition metal dopants | PLD | SSM[e] |
| | | Photocatalysis Sensors | Pentacene/(Sr, La)$TiO_3$ | PLD/MBE | AFM |
| NIMS | Dr. Toyohiro Chikyow<br>Dr. K. Tatsumura<br>Mr. T. Nagata | High-k Gate Dielectrics | $HfO_2$-$Al_2O_3$-$Re_2O_3$ | PLD | SMM[f] |
| | | Epitaxial Semiconductors | GaN/ZnO/$SiO_2$/Si | PLD | |

# Japan Visit, February 2004

| | | | | | |
|---|---|---|---|---|---|
| AIST | Dr. A. Yamamoto | Thermoelectrics[g] | $Sb_2Te_3$ – $SbBiTe_3$<br><br>Si-Ge | MBE<br><br>MBE | PF<br><br>PF |
| University of Tokyo | Prof. Mikk Lippmaa<br>Prof. Harold Hwang | Crystalline Oxides<br><br>Epitaxial Oxides<br><br>High Tc Superconductors | | PLD | RHEED, XRD |
| KEK | Dr. H. Kumigashira | Magnetic Resonance Devices | Epitaxial Manganate Superlattices | PLD | LEED, Synchrotron XPS[h] |
| Tohoku University | Prof. Masashi Kawasaki<br>Prof. A. Miyamoto<br>Mr. Tsukazaki<br>Mr. Ohtani<br>Dr. Yamada | Magnetic Oxides<br><br>UV Lasers, transparent semiconductors | $La_{1-x}Sr_xMnO_3/SrTiO_3$<br><br>$ZnO/Mg_xZn_{1-x}O$ | PLD<br><br>PLD | SSM<br><br>RHEED |

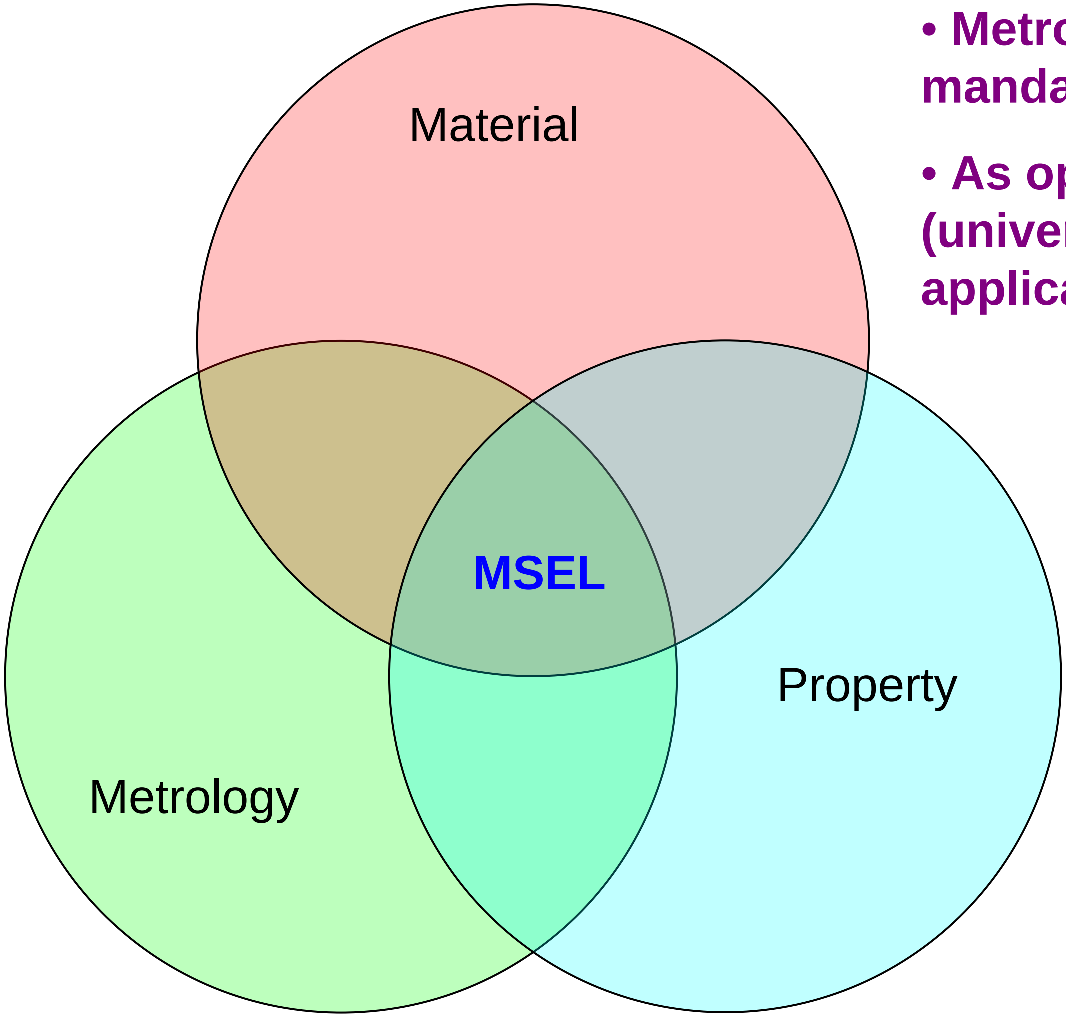
# Roles NIST/MSEL Could Play in Inorganic Combinatorial Materials Science

- Understanding combinatorial methodology as a:
  - method of materials optimization, development and discovery
  - means of experimentally verifying computed materials properties
  - tool for determining phase diagrams and other property data

# Combinatorial Material Systems Opportunities (Inorganic)

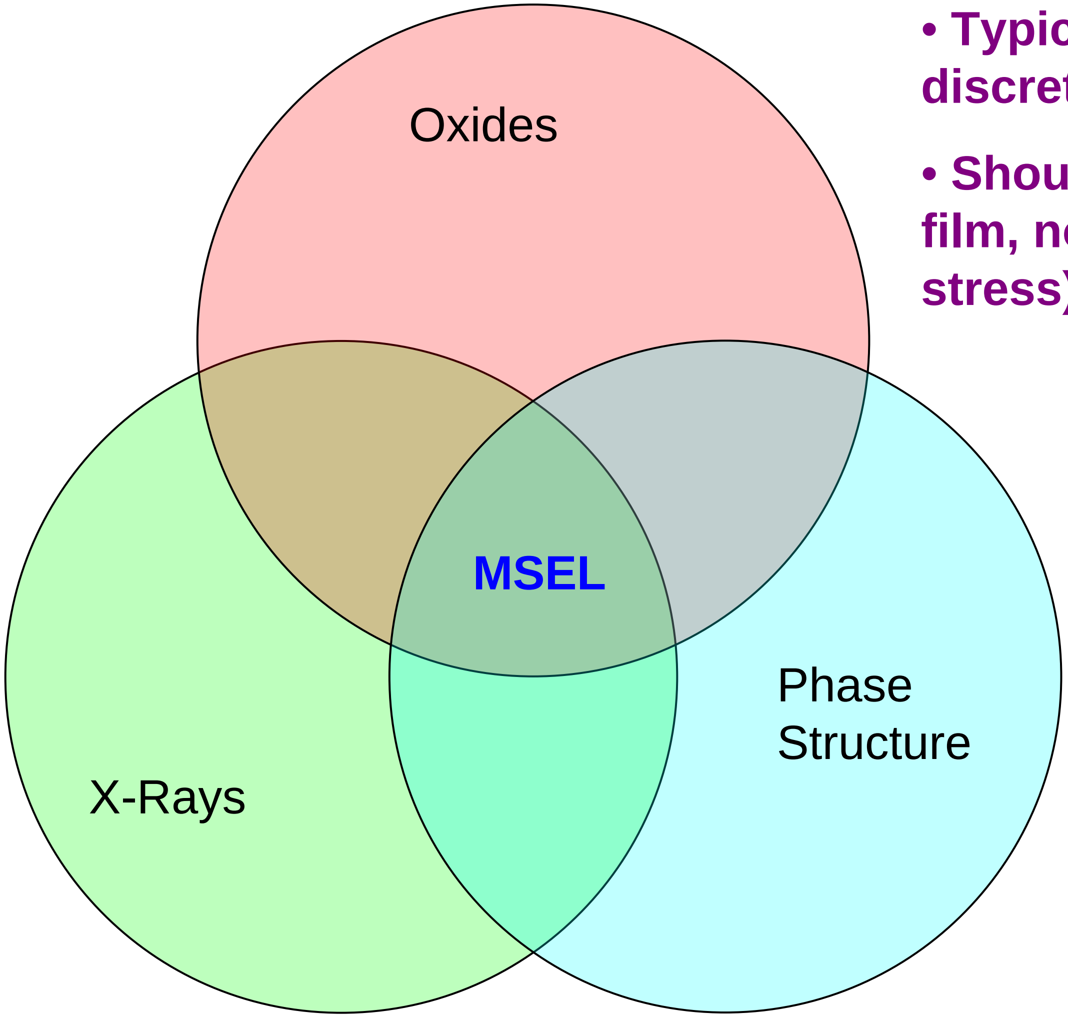
- Si Microelectronics
  - Metal gates
  - High-k gate dielectrics
  - FeRAMS
  - Magnetic memories
- Sensor Materials
- Thermoelectric Materials
- Transparent Semiconductors
- Magnetic Semiconductors
- Magnetic Shape-memory Alloys

# MSEL: Role of Combinatorial Methodology



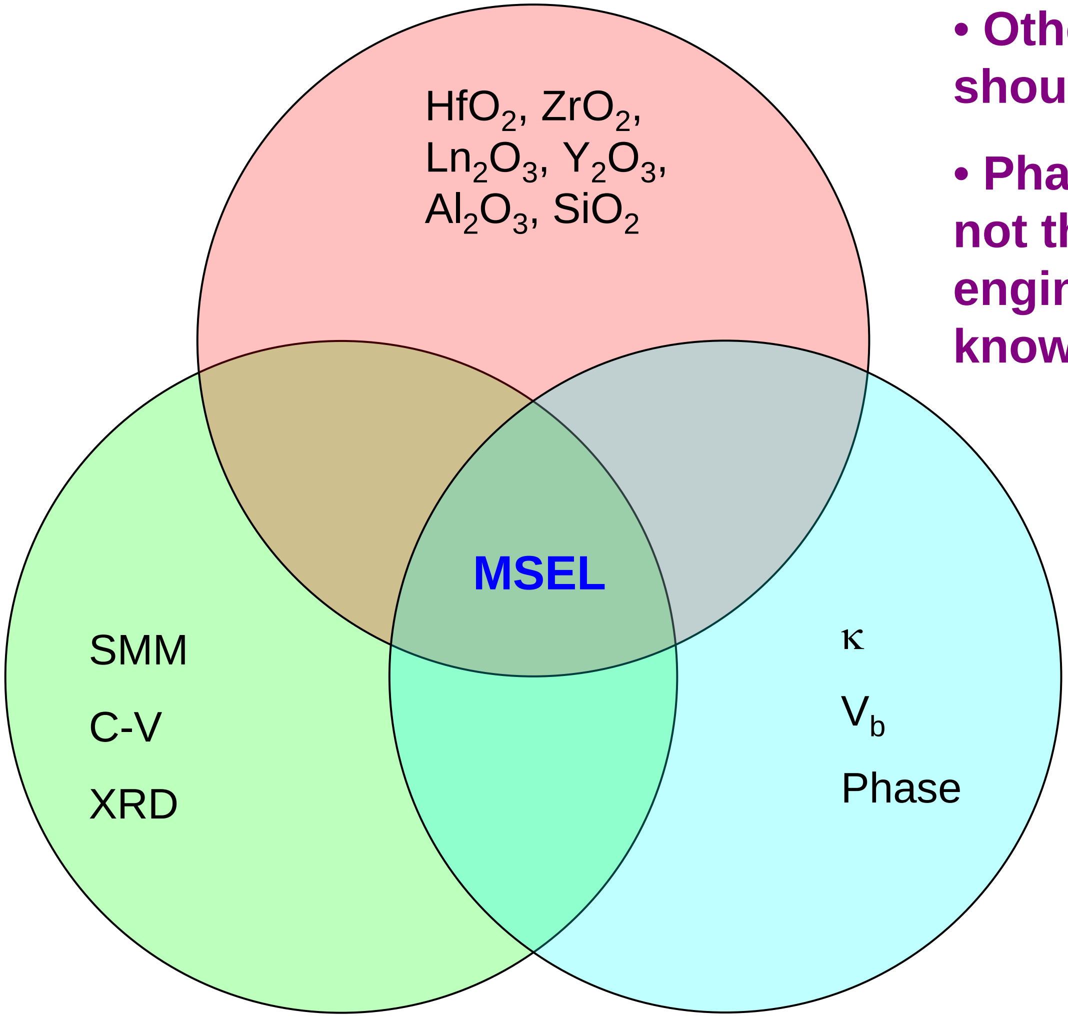

- Metrology is uniquely NIST's mandate
- As opposed to synthesis (university, industry), or application (industry, military)

# Phase Diagram: Typical NIST Product




- Typically accomplished using discrete, bulk samples
- Should also be done in the thin film, non-equilibrium state (e.g., stress), combinatorially

# Alternate Gate Dielectrics




- **Other property libraries should be developed**
- **Phase structure is generally not the first thing the "Intel" engineer or scientist wants to know**

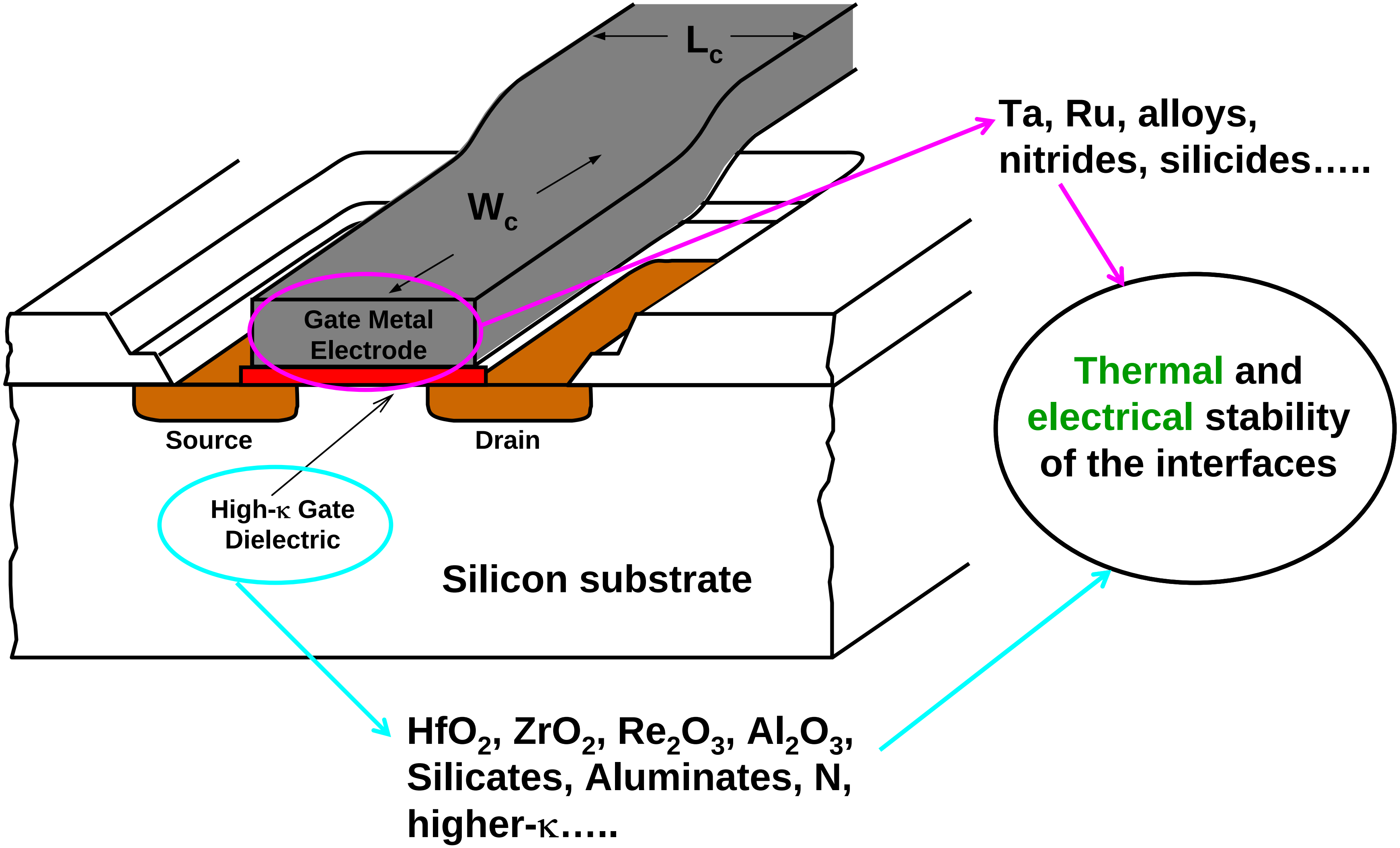
# Advanced Gate Stacks

- The 2003 ITRS states:

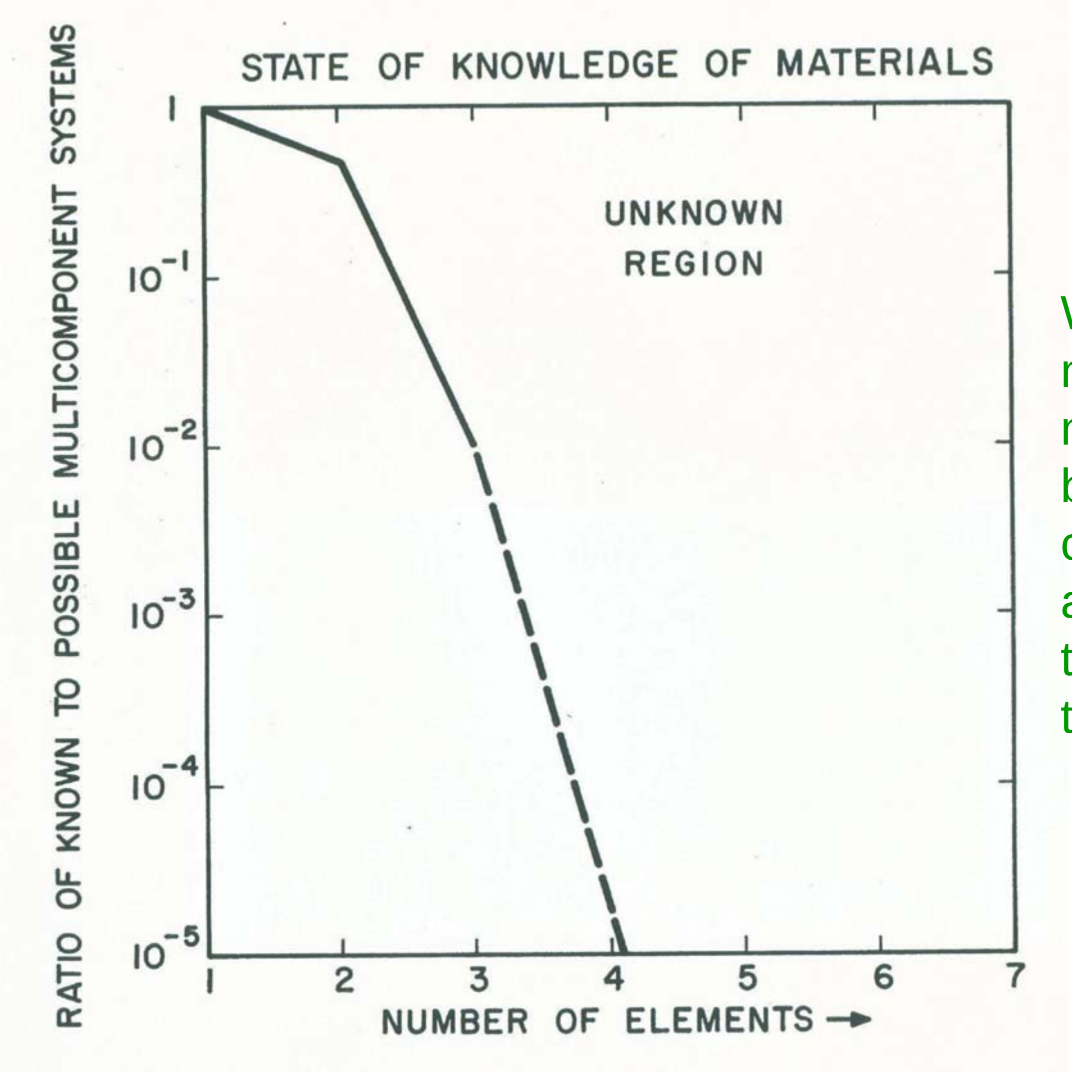
"We have entered the era of ***materials limited*** device scaling…The challenges associated with these ***diverse new materials***, and the control of the ***physical interfaces*** associated with these materials, constitutes the central theme of the front-end processing challenges… In no area is this issue ***more clear or urgent than in the MOSFET gate stack***".

- The advanced gate stack is a grand materials science and engineering challenge for International Sematech

# Complexity of the Advanced Gate Stack

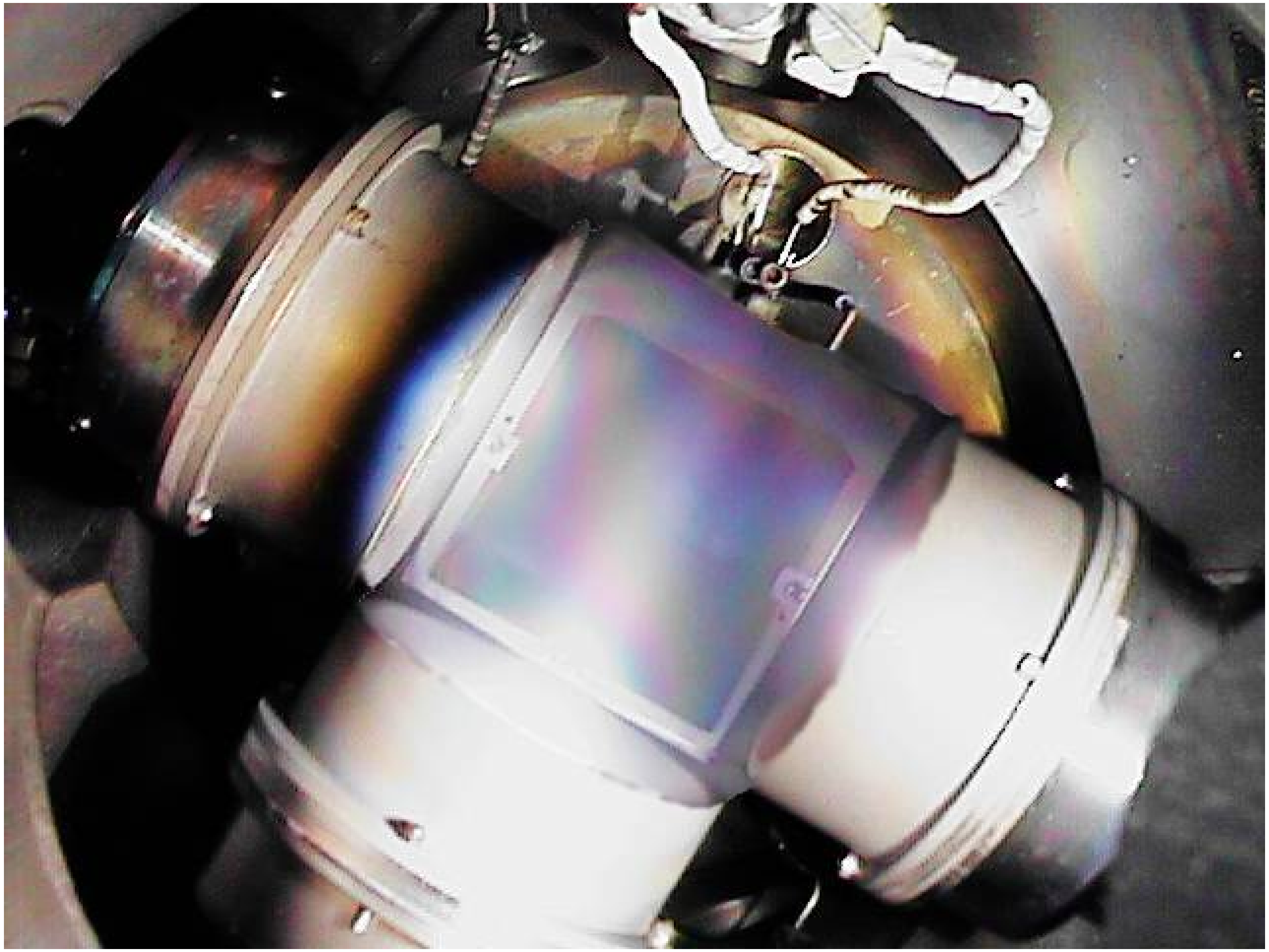


# Combinatorial Materials Science




Whatever one is trying to make, the choice of materials is often bewildering. Novel combinatorial approaches allow one to reduce the time and costs necessary to optimize results.

# Off-Axis Reactive Sputtering of High-$\kappa$ Gate Dielectrics



R. B. Van Dover

# "But that's not the way we'll make it…"

- Combinatorial methodology excels for:

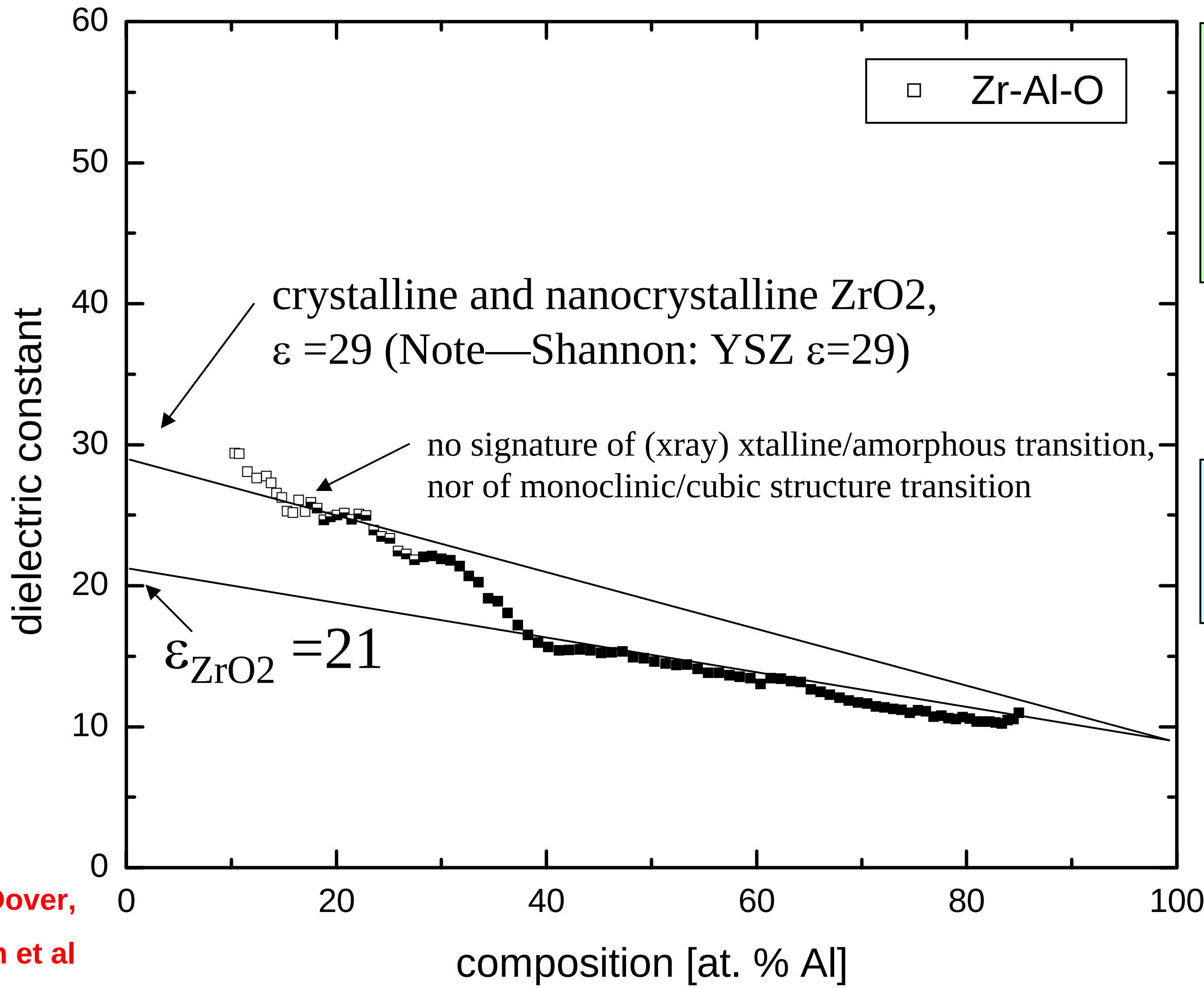
  *- Observation of trends ("slope" is more important than exact value of a property)*

  *- Screening, i.e., finding the "sweet spot" of the response surface*

  *- Measurement of structure-insensitive properties*

- Results must be benchmarked and carefully interpreted

# Zr-Al-O Dielectric Constant vs. Composition




Plotted here is the *median* dielectric constant at each composition

linear interpolation is accurate

$\varepsilon_{Al2O3} = 9$

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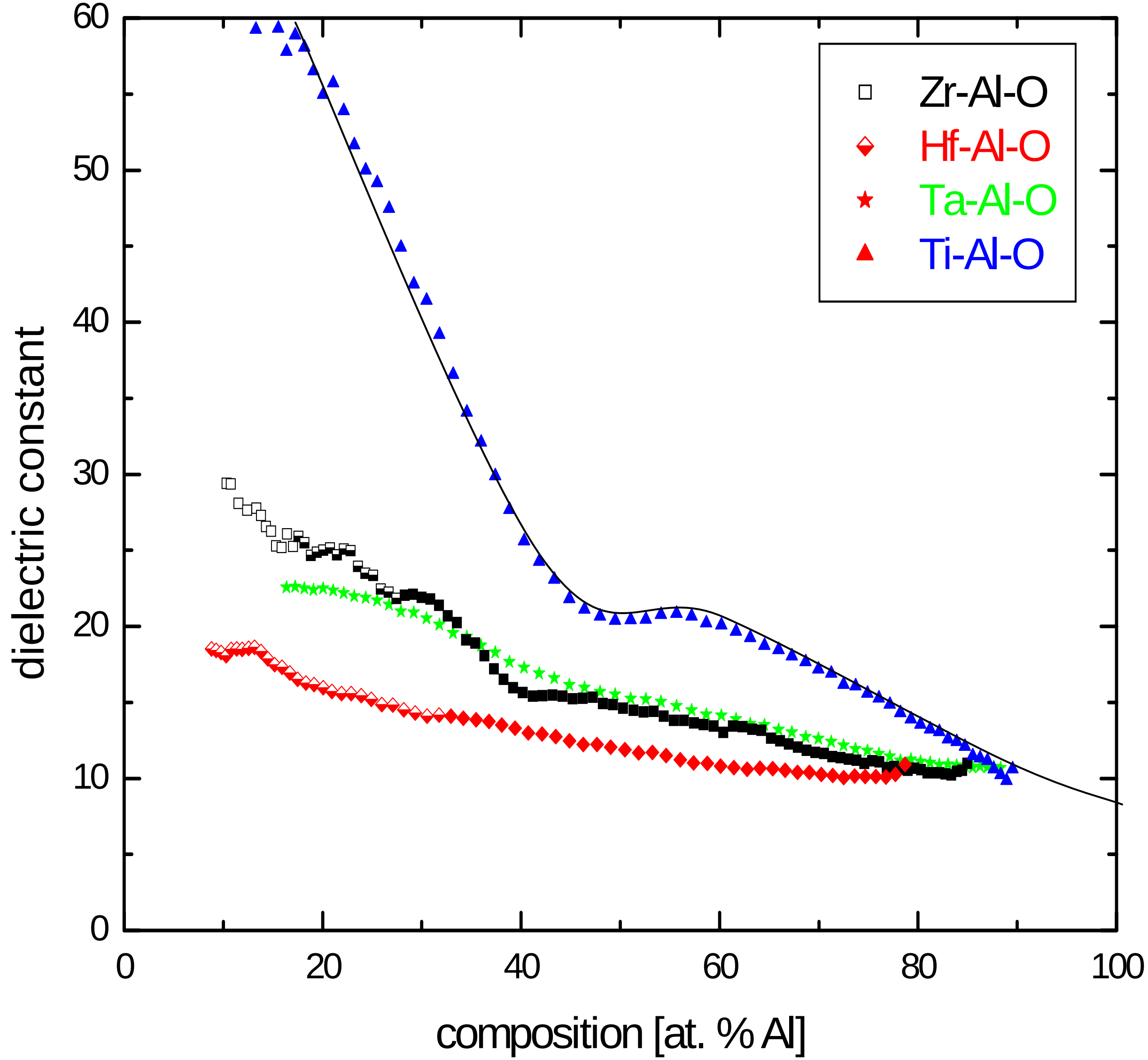
# Aluminates: Dielectric Constants




*One would not (or could not) explore all of these compositions with ALD!*

very nonlinear, addition of small [Al] sharply decreases ε

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# Design of Experiment

• Typical libraries:

- Ta-Ru-Si on Hf-O-N
- Ta-Si-N on high-$\kappa$ (newly identified)

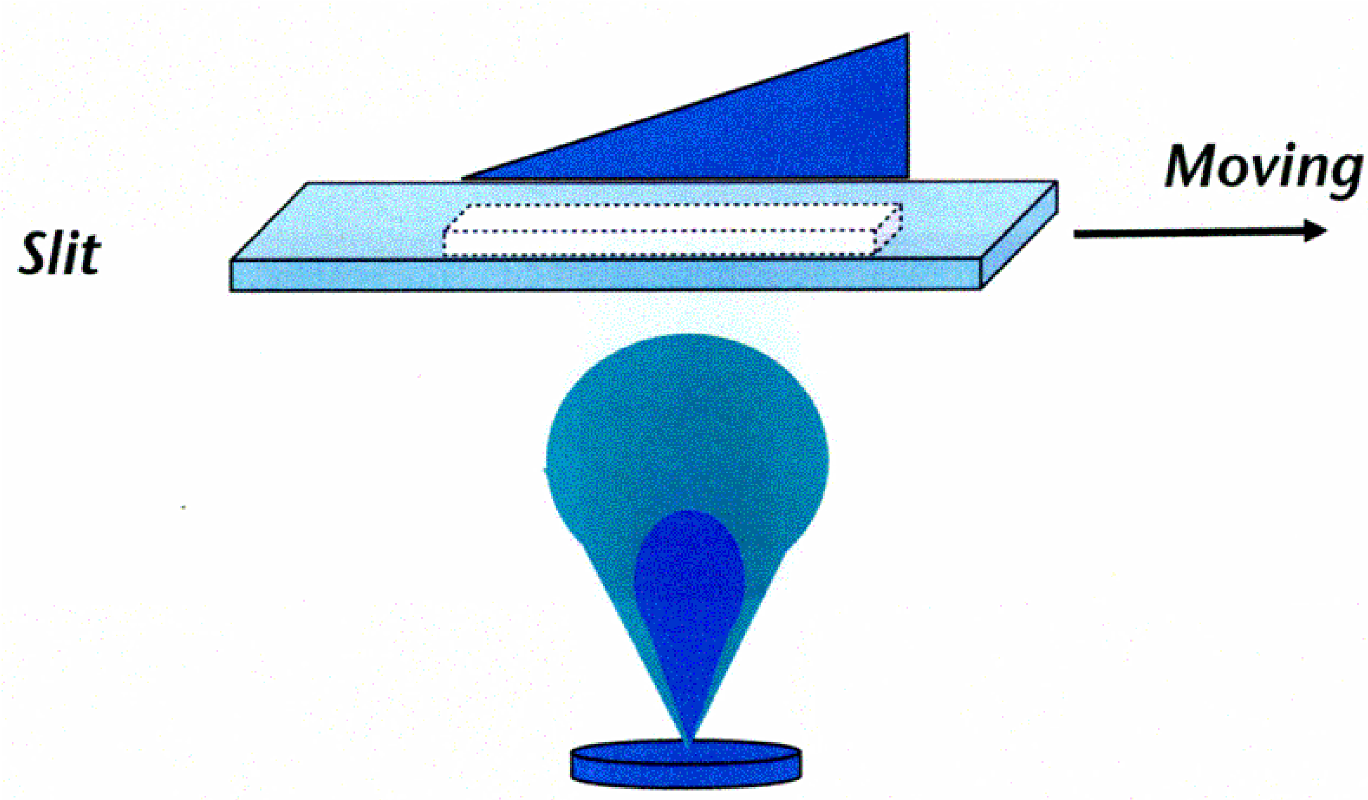
• What information (minimum) must we know about the advanced gate stack?

- ***thermal stability*** of the gate dielectric and metal gate layers and their interfaces (crystallization, interdiffusion, interfacial reactions….)
- ***electrical characteristics*** of the stack ($V_T$, $\Phi_b$, $Q_f$, $Q_{it}$….), and how are these properties affected by thermal treatment?

• What measurements will be made to characterize the gate stack?

- nanocalorimetry
- micro x-ray diffraction, electron backscatter diffraction
- C-V curves
- i-V curves
- conductance as a function of frequency
- gate metal work function, $\Phi_m$

# Compositional Gradient:
## Pulsed Laser Deposition (PLD)



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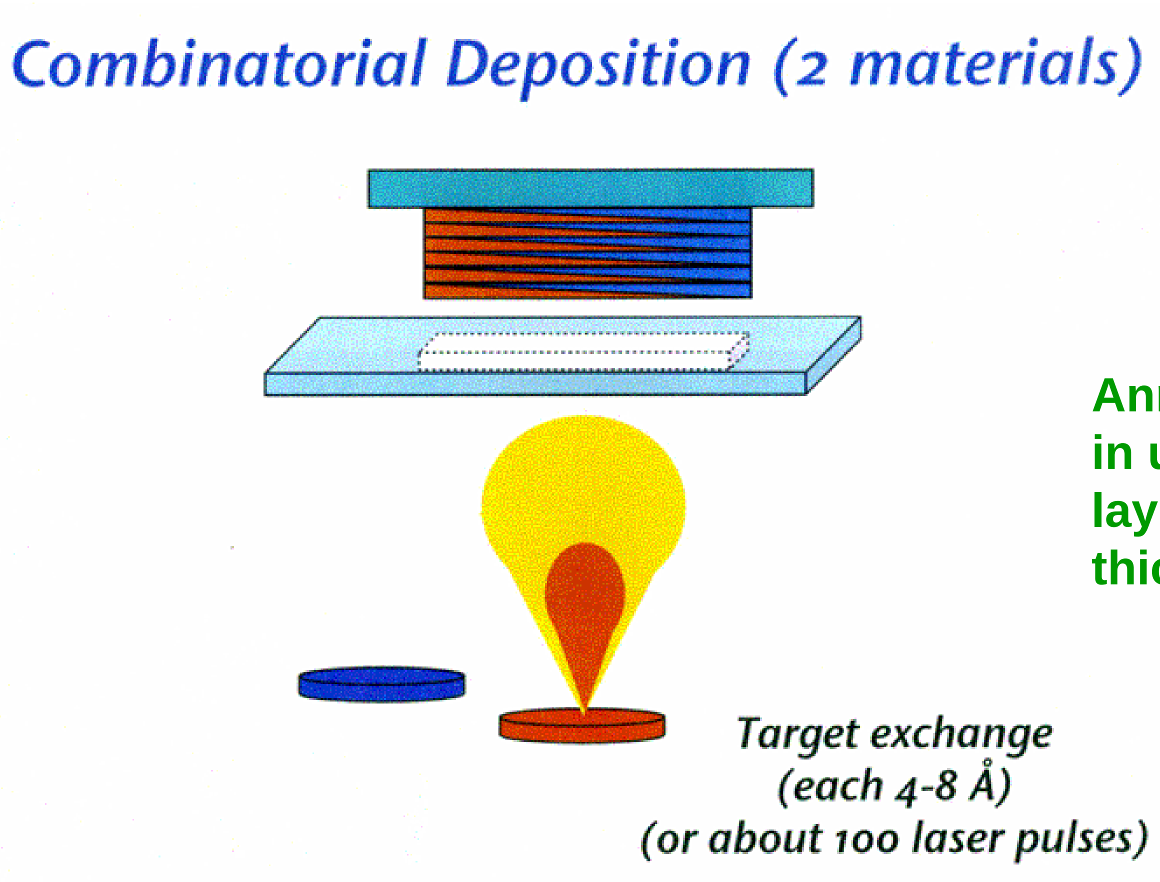
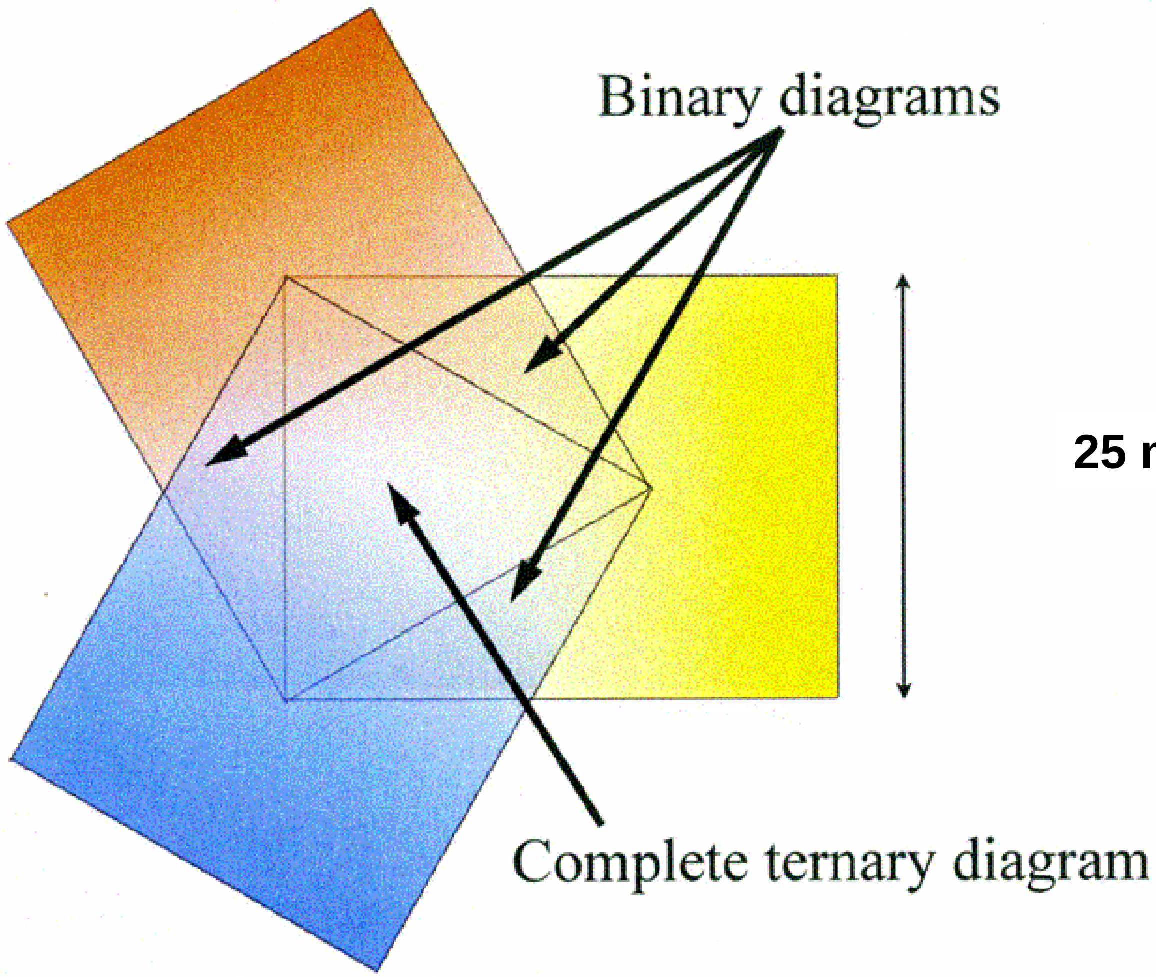



**Annealing results in uniform graded layer of any thickness**

# Ternary System




25 mm

# Combinatorial Analysis Techniques: Advanced Gate Stacks

| Quantity or Property | Measurement | Technique | Comments |
|---|---|---|---|
| Phase change | Differential temperature | Nanocalorimetry | |
| Crystallinity | Diffracted intensity | Electron backscatter diffraction | |
| Crystal structure | Diffracted intensity | Micro x-ray diffraction | |
| Threshold voltage | Flatband voltage | C-V curves | |
| Barrier height for tunneling | Current | i-V curves | |
| Fixed Charge | Conductance | Conductance = f($\omega$) | |
| Interfacial States | Metal work function | Kelvin probe | Knowing $V_{fb}$ and $\Phi_s$ |



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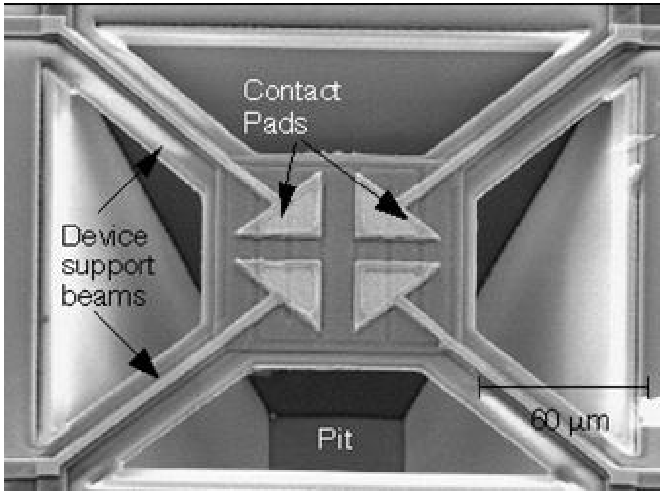
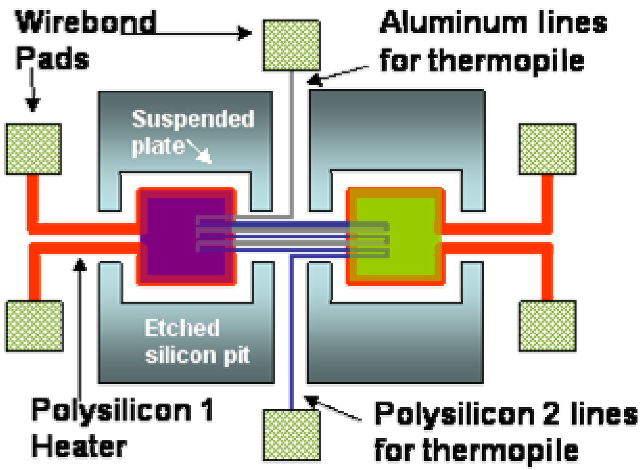
# Nanocalorimetry




single microhotplate


4-element microhotplate array
for gas microsensor prototypes




microcalorimeter schematic

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